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# Comparison of Cadmium and Phosphate Concentrations during Red Tide versus no Red Tide Conditions

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**ABSTRACT**

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Red tide events have been more common in recent years along the Pacific coast of Baja California, México, and the US. Even though that the organisms causing them sometimes do not produce harmful substances and are therefore considered as non-toxic, toxic trace metals, like Cd, can be increased to a significant level. Dissolved Cd and $PO_4$ were measured in Todos Santos Bay, Mexico, during a red tide algal bloom (August, 2005) and with no red tide present (May, 2006). The average concentrations of dissolved Cd and $PO_4$ (1.38 nM and 1.40 μM, respectively) in 2005 were significantly higher than 2006 (Cd: 0.37 nM and $PO_4$: 0.45 μM) when no red tide was present. Pearson correlation between dissolved Cd and $PO_4$ in 2005 was lower ($r$ = 0.601, $P$ = 0.018), but significant, than that presented in 2006 ($r$ = 0.880, $P$ < 0.001). The extremely high Cd concentrations found in 2005, which have been only reported in highly contaminated areas, are presumably due to the extensive red tide that occurred during that year. A small set of data on phytoplankton abundance and dissolved Cd indicates that dinoflagellates are playing a role in the high Cd concentrations obtained during red tide since the correlation between Cd concentration and dinoflagellates abundance was high ($r$ = 0.984, $P$ < 0.001). The mechanism by which this is accomplished is not known.

**ADITIONAL INDEX WORDS:** *dinoflagellates, Todos Santos Bay, Mexico*

## INTRODUCTION

During the last few years very large red tide algal blooms have been occurring along the Pacific coasts of México and USA. During the summer of 2005 Lares et al. (2008) reported high concentrations of cadmium and phosphates, during a large red tide event, compared to previous reported concentrations in Todos Santos Bay (TSB). TSB is located in the northwest area of México (Figure 1) and it is in open communication with the Pacific Ocean which largely determines its water properties. In this area upwelling events occur very frequently and thus the concentration of different properties are those of the subsurface waters. In particular, Cd and $PO_4$ are very well known to be good upwelling indicators (Bruland et al., 1978; van Geen and Husby, 1996) with maximum concentrations reported along the Pacìfic coast of 1.0 nM for Cd (Takesue et al., 2004) and 2.5 μM for $PO_4$ (van Geen and Luoma, 1993). In TSB the maximum concentrations of Cd and $PO_4$ found in normal conditions (i.e., without the presence of red tides) has been 0.51 nM for Cd (Lares et al., 2008) and 1.0 μM for $PO_4$ (Espinosa-Carreon et al., 2001). However, during the 2005 red tide algal bloom, TSB reached unprecedented high values of Cd (2.15 nM) and $PO_4$ (5.11 μM) (Lares et al., 2008).

The aim of this study is to compare the Cd and $PO_4$ concentrations in Todos Santos Bay with and without the presence of red tide algal blooms.

## MATERIAL AND METHODS

Seawater samples were collected along fifteen stations within TSB on August 10, in 2005 (data previosly reported by Lares et al., 2008) and May 5, in 2006. An additional cruise on August 7, 2008 was performed to take samples for phytoplankton abundance besides the seawater samples taken for Cd analyses. Details of sampling protocol for 2005 and 2006 cruises can be found in Lares et al. (2008). Briefly, samples for Cd analysis were taken following a “clean-hands/dirty-hands” protocol using previously cleaned (trace-metal) bottles which were double zip-lock bagged. The samples were taken with 2 m long PVC sampling device which permit the opening and closing of the bottles 1 m below the surface. The 2008 cruise was aboard the R/V Francisco de Ulloa and 20 samples covering the bay were taken with Go-Flo (General Oceanic) bottles at 10 m depth. Water samples from these bottles were taken into pre-cleaned 1 L LDPE bottles in a Class-100 Environment laminar flow clean-air bench installed on board. Seawater filtering and pre-concentration of the samples were carried out at the laboratory in a Class-100 trace-metal clean room. Seawater from the 2005 sampling was pre-filtered through a pre-cleaned (acid washed) 1 µm Nucleopore filter (47 mm diam.), since the amount of particles due to the red tide plugged the 0.45 µm (47 mm diam. Nucleopore) filters very quickly. Dissolved Cd in this study is defined as the fraction that passes through a 0.45 µm filter. Filtered seawater was acidified (pH < 2.0) with Ultrex-

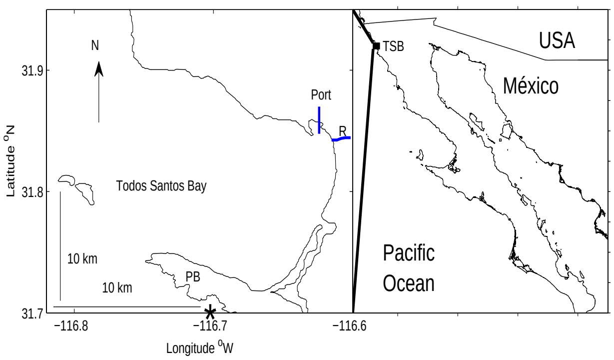


Figure 1. Study area. The line with the label R stands for a seasonal creek. The asterisk to the south of Punta Banda (PB) is Puerto Escondido where some data is reported here.

grade nitric acid, pre-concentrated using the Chelex-100® (Bio-Rad Laboratories, Richmond, CA) ion exchange technique (BRULAND et al., 1979), and quantified by graphite furnace atomic absorption spectrometry (GF-AAS; AAnalyst 600, Perkin-Elmer Inst.), using stabilized platform techniques and the method of standard additions to correct for matrix interferences. The accuracy of the analytical protocol was 110 % based on the analysis of the standard reference material CASS-3 (Canadian Research Council Canada). The variation of replicate analyses was < 10 %. The procedural blank was 0.04 nM ± 0.02 (n = 4). Phosphate concentrations were determined with a Skalar San Plus System II auto-analyzer by measuring the absorbance induced by chromatic complexes (EATON et al., 2005).

## RESULTS

A summary of the concentrations of Cd and $PO_4$ is shown in Table 1. Average Cd concentrations in 2005 was almost 4 times higher than in 2006 while $PO_4$ was 3 times higher. Student *t*-tests showed that Cd and $PO_4$ concenctrations were significantly higher in 2005 than in 2006 (Cd: $t = 5.05$, $P < 0.001$; $PO_4$: $t = 2.82$, $P = 0.009$). The variability of both variables (measured as the standard deviation) was also higher in 2005 as compared to 2006. The Cd and $PO_4$ spatial distributions for the two sampling periods are shown in Figure 2. A tendency for higher concentrations towards the coast (East side) can be appreciated for both Cd and $PO_4$ in both years. However, in 2005 there is also a marked increase of both variables to the northeast of the islands. Pearson correlation between dissolved Cd and $PO_4$ in 2005 was lower ($r = 0.601$, $P = 0.018$), but significant, than that presented in 2006 which was highly significant ($r = 0.880$, $P < 0.001$) (Figure 3). The slope for

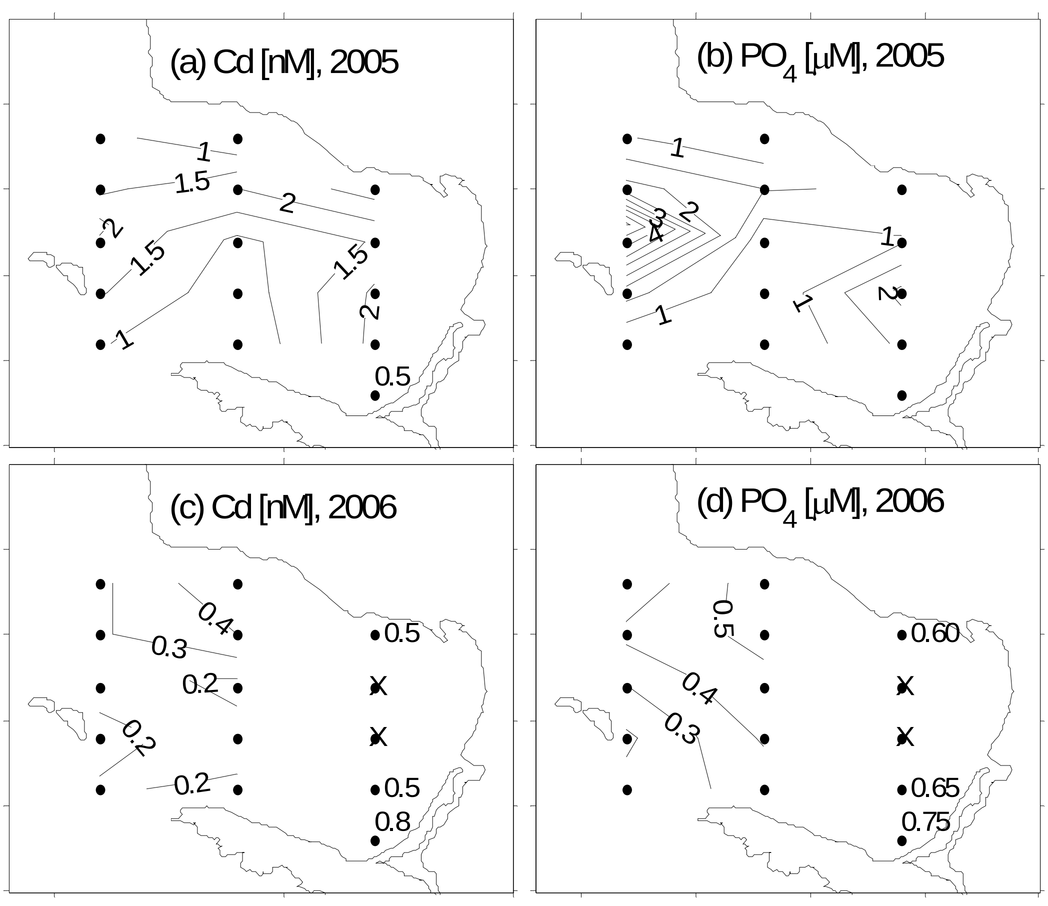


Figure 2. Spatial distribution Cd and $PO_4$ for 2005 and 2006.

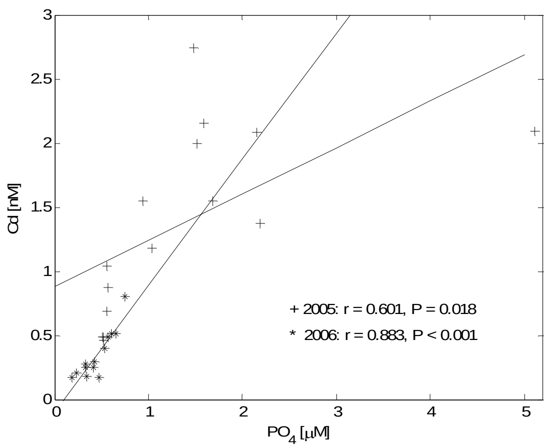


Figure 3. Cd vs $PO_4$ correlation for 2005 (+) and 2006 (*) samplings.

the Cd: $PO_4$ relationship for 2005 (Cd = 0.88 + 0.36 x $10^{-3}$ $PO_4$) was lower than for 2006 (Cd = -0.09 + 0.98 x $10^{-3}$ $PO_4$).

## DISCUSSION

Cd and $PO_4$ concentrations in TSB were higher during August 2005 when a long lasting (April to September) bloom of dinoflagellates, fully documented by PEÑA-MANJARREZ et al. (2008), was present. These high values are above those previously reported for TSB (Cd: 0.10-0.16 nM, SAÑUDO-WILHELMY and FLEGAL, 1996; $PO_4$: 0.5-1.0 µM, ESPINOSA-CARREON et al., 2001) even for coastal influenced areas inside the bay (Cd: 0.51 nM; LARES et al., 2008). However, in 2006 the concentrations of these variables were significantly lower and no evidence of red tide was found. These Cd and $PO_4$ concentrations were in the same order of magnitude of those found in the Pacific coast (Cd: 0.1-1.0 nM, TAKESUE et al., 2004; $PO_4$: 0.5-2.5 µM, van GEEN and LUOMA, 1993) where upwelling events are frequent. The variability in the Cd and $PO_4$ concentrations in 2005 was also higher than 2006 probably reflecting the patchiness of the red tide.

The spatial variability of Cd and $PO_4$ in 2005 and 2006 (Figure 2) was similar, both showing higher concentrations near the coast. In 2005 there was also a marked increase of both variables to the northeast of the islands which is explained by a shallow bank that induces interal tides and vertical mixing (LARES et al., 2008). This physical process probably produced a trap for the dinoflagellates which coupled with remineralization due to the long lasting red tide, concentrated the dissolved Cd. Cd and $PO_4$ were highly correlated in both samplings. The correlation was stronger in 2006 than in 2005 (see Results). Also, the relationship Cd:$PO_4$ was lower in 2005 than in 2006. This can be reflecting the preferential removal of Cd versus $PO_4$ by phytoplankton (de BAAR et al., 1994) which was more abundant in 2005 than in 2006.

The high Cd concentrations found in 2005 seems to be related to high dinoflagellate abundance. Few available data of dissolved Cd and phytoplankton abundance for 2006 (Valdez-Márquez, 2008, Programa de Monitoreo de Maricultura del Norte, Ensenada, México, unpublished report) from samples taken inside TSB and Puerto Escondido (outside TSB, see Figure 1) were combined with the data obtained from the 2008 cruise (Table 2). These data reflects the relationship of dinoflagellate abundance with dissolved Cd concentrations. The correlation between these two variables was highly significant ($r$ = 0.984, $P$ < 0.001). Correlation between diatoms abundance and Cd concentration, however, was not significant ($r$ = -0.213, $P$ = 0.685). Segovia-Zavala et al. (1998) also found high Cd concentrations related to high concentrations of chlorophyll *a* in a coastal upwelling zone close to the USA-Mexico border. However, the Cd concentrations reported in their work (0.14-0.17 nM) were an order of magnitude lower than the ones encountered in the present study for 2005. There was no report of the phytoplankton species.

A final comment is that even tough the frequent red tide events, including that of 2005, have been considered as non-toxic, the high Cd concentrations found should be of concern since this metal can be highly concentratedin filter feeders like mussels and oysters (from 10 000 to 100 000 times, respectively, MARTINCIC et al., 1984) that are being cultivated in the bay.

Table 1: Basic statistics of the variables measured.

| | Mean | Std dev | Max. | Min. |
|---|---|---|---|---|
| Cd 2005 (nM) | 1.38 | 0.72 | 2.74 | 0.46 |
| $PO_4$ 2005 (µM) | 1.40 | 1.19 | 5.11 | 0.51 |
| Cd 2006 (nM) | 0.35 | 0.19 | 0.80 | 0.17 |
| $PO_4$ 2006 (µM) | 0.45 | 0.17 | 0.75 | 0.18 |

## CONCLUSION

Red tide events have shown to increase environmental Cd and $PO_4$ concentrations up to 4 and 3 times, respectively. High correlation with dinoflagellate abundance and not with diatoms means that this phenomenon is taxonomic specific. The mechanism by which this is accomplished needs further investigation.

## LITERATURE CITED


BRULAND, K.W.; KNAUER, G.A., and MARTIN, J.H., 1978. Cadmium in the northeast Pacific waters. *Limnology and Oceanography*, 23, 618-625

BRULAND, K.W.; FRANKS, R.P.; KNAUER, G.A., and MARTIN, J.H., 1979. Sampling and analytical methods for the determination of copper, cadmium, zinc and nickel at the nanogram per liter level in sea water. *Analytical Chemical Acta*, 105,203-245

de BAAR, H.J.W.; SAAGER, P.M.; NOLTING, R.F., and van der MEER, J. 1994. Cadmium versus phosphate in the world ocean. *Marine Chemistry*, 46,261-281

EATON, A.D.; CLESCERI, L.; RICE, E.; GREENBERG, A., and


Table 2: Cd concentrations and phytoplankton abundance. PE stands for Puerto Escondido (see location in Figure 1). The 2008 data is the average of 20 samples taken at 10 m depth.

| Location | Date | Cd (nM) | Diatoms (cells $L^{-1}$) | Dinoflagellates (cells $L^{-1}$) |
|---|---|---|---|---|
| TSB | 05/09/06 | 2.05 | 8 000 | 237 000 |
| PE | 06/01/06 | 0.49 | 19 000 | 66 500 |
| PE | 06/30/06 | 0.01 | 84 000 | 10 000 |
| PE | 07/31/06 | 0.90 | 181 500 | 76 000 |
| PE | 09/01/06 | 0.25 | 154 700 | 7 400 |
| TSB | 08/07/08 | 0.11 | 12 823 | 2480 |

FRANSON, M. (eds.), 2005. Standard Methods for Examination of Water and Wastewater. 21th. Edition. APHA, AWWA, WEF. 1325 pp.

ESPINOSA-CARREON, T.L.; GAXIOLA-CASTRO, G.; ROBLES-PACHECO, J.M., and NÁJERA-MARTINEZ, S., 1993. Temperature, Salinity, Nutrients and Chlorophyll *a* in coastal waters of the southern California Bight. *Ciencias Marinas*, 27,397-422

LARES, M.L.; MARINONE, S.G.; RIVERA-DUARTE, I.; BECK, A., and SAÑUDO-WILHELMY, S., 1993. Spatial variability of trace metals and inorganic nutrients in surface waters of Todos Santos Bay, México in summer of 2006 during a red tide bloom. *Archives of Environmental Contaminations and Toxicology*, doi: 10.1007/s00244-008-9210-x.

MARTINCIC, D.; NURNBERG, H.W.; STOEPPLER, M., and BRANICA, M., 1984. Bioaccumulation of heavy metals by bivalves from Lim Fjord (North Adriatic Sea). *Marine Biology*, 81,177-188

PEÑA-MANJARREZ, J.L.; GAXIOLA-CASTRO, G., and HELENES-ESCAMILLA, J., 2008. Environmental factors influencing the variability of *Lingulodinium polyedrum* and *Scrippsiella trochoidea* (Dinophyceae) cyst production. *Ciencias Marinas*, in press.

SAÑUDO-WILHELMY, S. and FLEGAL, A.R., 1996. Trace Metal Concentrations in the Surf Zone and in Coastal Waters off Baja California, Mexico. *Environmental Science Technology*. 30,1575-1580

SEGOVIA-ZAVALA, J.A.; DELGADILLO-HINOJOSA, F., and ALVAREZ-BORREGO, S., 1998 Cdmium in the coastal upwelling area adjacent to the California-Mexico border. *Estuarine, Coastal and Shelf Science*, 46,475-481

TAKESUE, R.K, van GEAN, A.; CARRIQUIRI, J.D.; ORTIZ, E.; GODINEZ-HORTA, L.; GRANADOS, I.; SALDIVAR, M.; ORTLIEB, L.; ESCRIBANO, R.; GUZMAN, N.; CASTILLA, J.C.; VARAS, M.; SALAMANCA, M., and FIGUEROA, C., 2004. Influence of coastal upwelling and El Niño-Southern Oscillation on nearshore water along Baja California and Chile: Shore-based monitoring during 1997-2000. *Journal of Geophysical Research*, 109,C03009

van GEEN, A. and HUSBY, D.M., 1996. Cadmium in the California current system: tracer of past and present upwelling. *Journal of Geophysical Research*, 101,3489-3507

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